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(56) Documents cited

GB 0994479 A GB 0860135 A GB 0845206 A
GB 0820266 A EP 0368270 A EP 0102709 A1

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(54) A process for the production of elastomeric Polyurethanes, particularly in the form of shoe soles

(57) In the production of elastomeric polyurethanes, more particularly in the form of shoe soles, using a polyurethane reaction mixture, low-stability or non-storable premixes of polyol and crosslinking agent can be avoided and immediate changes can be made to the crosslinking agent without any losses if the isocyanate, polyol and crosslinking agent are separately delivered to the mixing chamber. Optional catalysts and/or blowing agents can also be separately delivered to the mixing chamber. The processing temperature of the polyol component may be 60° to 150°C.

GB 2 257 150 /

A PROCESS FOR THE PRODUCTION OF ELASTOMERIC POLYURETHANES,
MORE PARTICULARLY IN THE FORM OF SHOE SOLES

This invention relates to a process for the production of elastomeric polyurethanes, more particularly in the form of shoe soles, by reaction of a polyurethane reaction mixture of polyol, isocyanate, crosslinking agents and, 5 optionally, catalysts, blowing agents and other additives which are mixed together, as known from EP-A-0 368 270.

The following starting components are used for the production of the elastomeric polyurethanes:

- 10 1. Aromatic polyisocyanates of the type described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, for example those corresponding to the following formula:



in which

n = 2 to 4, preferably 2, and

- 20 Q is an aromatic hydrocarbon radical containing 6 to 15 and preferably 6 to 13 carbon atoms, for example polyisocyanates of the type described in DE-OS 28 32 253, pages 10 to 11.

In general, it is particularly preferred to use commercially readily obtainable polyisocyanates, for 25 example 2,4- and 2,6-tolylene diisocyanate and mixtures of these isomers ("TDI"), polyphenyl polymethylene polyisocyanates of the type obtained by phosgenation of aniline/formaldehyde condensates ("crude MDI") and polyisocyanates containing carbodiimide groups, urethane groups, aliphatic groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"), more particularly the modified polyisocyanates derived from 2,4- and/or 2,6-

tolylene diisocyanate and from 4,4'- and/or 2,4'-diphenyl methane diisocyanate.

2. Another starting component is the "polyol" component,
5 i.e. for example polyesters containing at least two isocyanate-reactive hydrogen atoms and having a molecular weight of generally 400 to 10,000. In addition to compounds containing amino groups, thiol groups or carboxyl groups, polyesters of the type in question are compounds containing
10 hydroxyl groups, more particularly compounds containing 2 to 8 hydroxyl groups, especially those having a molecular weight in the range from 1,000 to 8,000 and preferably in the range from 2,000 to 4,000, for example compounds containing at least 2, generally 2 to 8 and preferably 2 to 4
15 hydroxyl groups, of the type known per se for the production of homogeneous and cellular polyurethanes and described, for example, in DE-OS 28 32 253, pages 11 to 18.

According to the invention, polyethers, polycarbonates, polylactones and polyamides containing at least 2
20 hydroxyl groups and having a molecular weight in the range from 400 to 10,000 may also be used.

3. Other starting components are crosslinking agents, i.e. compounds containing at least two isocyanate-reactive
25 hydrogen atoms and having a molecular weight of 18 to 399. In this case, too, the compounds in question are compounds containing hydroxyl groups and/or amino groups and/or thiol and/or carboxyl groups, preferably compounds containing hydroxyl groups and/or amino groups which serve as crosslinking agents. These compounds generally contain 2 to 8 and preferably 2 to 4 isocyanate-reactive hydrogen atoms. Examples of such compounds can be found in DE-OS 28 32 253, pages 19 to 20.

35 4. Blowing agents, such as water or readily volatile

compounds, are optionally used.

5. Flameproofing agents known per se are optionally used.

5 6. Auxiliaries and additives known per se, such as emulsifiers and stabilizers, are optionally used. Preferred emulsifiers are those based on alkoxylated fatty acids and higher alcohols.

10 Suitable stabilizers are, above all, polyether siloxanes, particularly water-soluble types. The structure of these compounds is generally such that a copolymer of ethylene oxide and propylene oxide is attached to a polydimethyl siloxane unit. Stabilizers of this type are described, for example, in US-PSS 2,834,748, 2,917,480 and 15 3,629,308. Catalysts known per se from polyurethane chemistry, such as tertiary amines and/or organometallic compounds, may also be used.

20 Reaction retarders, for example compounds showing an acidic reaction, such as hydrochloric acid or organic acid halides, and cell regulators known per se, such as paraffins or fatty alcohols or dimethyl polysiloxanes; pigments or dyes; stabilizers against the effects of ageing and weathering; plasticizers; fungistatic and bacteriostatic agents and fillers, such as barium sulfate, kieselguhr, 25 carbon black or whiting, may also be used.

30 Further examples of surface-active additives and foam stabilizers, cell regulators, reaction retarders, stabilizers, flameproofing agents, plasticizers, dyes and fillers, fungistatic and bacteriostatic agents which may optionally be used in accordance with the invention and information on the use of these additives and their mode of action can be found in Kunststoff-Handbuch, Vol. VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, München 35 1966, for example on pages 103 to 113.

Shoe soles of elastomeric polyurethanes are generally produced by direct molding onto the upper material. In the preparation of the reaction mixture, a crosslinking agent, a catalyst and a blowing agent have hitherto been premixed with the polyol component. The resulting premix is subsequently mixed with isocyanate in a mixing head. The reaction mixture reacts out to form a material which can be made compact to cellular and flexible to rigid, depending on the ratio of polyol to crosslinking agent.

Since the premix in question can only be stored for a limited time, as can be seen from EP-A-0 368 270, column 1, lines 29 to 50, attempts have already been made - according to that document - to eliminate the poor stability in storage by only carrying out the premixing operation after the liquid level in the silo containing a day's supply of molding material has fallen below the predetermined minimum level, a limited refill volume being produced in each premixing operation and passing through a heat exchanger before delivery to the silo for heating to a temperature corresponding to the temperature of the silo. However, this concept does not eliminate all disadvantages. For example, that part of the installation which carries the mixture of polyol and crosslinking agent has to be completely emptied and rinsed in the event of prolonged stoppage times, for example at weekends, because the chemical reaction between the polyol and crosslinking agent takes place from the outset, so that the transition from "good" to "totally unuseable" is gradual and satisfactory production is only possible when final processing takes place immediately after premixing.

However, the most serious disadvantage is that it should be necessary at all to prepare a premix of polyol and other components, of which the crosslinking agent plays the most important part. This is because the crosslinking agent determines the degree of hardness of the elastomer or

rather the shoe sole and this degree of hardness often has to be changed during production. In the event of such changes, residues of the premix normally remain behind and, unless they can be used in a reasonable time, become
5 unuseable on account of the reactions taking place.

Accordingly, the problem addressed by the present invention was to provide a process for the production of elastomeric polyurethanes, particularly in the form of shoe soles, which would eliminate the need to empty the polyol
10 side of the installation in the event of prolonged stoppages and which, in addition, would enable the degree of hardness of the elastomer to be changed immediately without any losses.

According to the invention, the solution to this problem is characterized in that the components polyol,
15 isocyanate and crosslinking agent are fed through separate lines to a mixing chamber and are only combined and mixed together in this mixing chamber.

Compared with the earlier procedure, this measure eliminates losses of mixture of polyol and crosslinking agent and also additional labor because no premature reactions can take place. Changes can now be made to the polyol component, which determines the index, and to the crosslinking component, which is responsible for the degree
25 of hardness, independently of one another with immediate effect.

The separate delivery of individual components, such as dyes for example, to the mixing chamber is basically known. However, in the production of elastomeric polyurethanes and particularly in the production of shoe soles,
30 there were prejudices against directly delivering the crosslinking agent to the mixing chamber. Since, on the one hand, shoe soles are relatively small moldings and, on the other hand, the crosslinking component is very small in relation to the polyol component, it was regarded as im-

possible to achieve exact dosage of these small quantities from the first to the last millisecond. In addition, homogeneous distribution of such small quantities was only considered to be possible by premixing in the polyol. In other words, it was believed that direct introduction into the mixing chamber would result in inadequate mixing and, hence, in a sub-optimal end product in this particular application.

In a preferred embodiment, catalysts and/or blowing agents are also separately delivered and are only mixed with the other components in the mixing chamber.

By virtue of their direct introduction into the mixing chamber, changes can also be directly made to these additives without any losses. Changes in the catalyst component result in changes in the reaction time while changes in the blowing agent component affect the pressure inside the mold. Relatively high foaming pressures have to be applied in particular in the production of shoe soles with difficult contours in order to ensure that the exact contours of the mold cavity are reproduced.

Overcoming these prejudices has surprisingly resulted in further unforeseeable possibilities, namely:

The processing temperature of the polyol can be significantly increased which provides for a considerable reduction in viscosity and hence for a considerable improvement in the quality of mixing. Whereas, hitherto, processing temperatures of 25 to 50°C have been typically applied, polyol processing temperatures of, preferably, 60 to 150°C and, more preferably, around 110°C can be applied in the new process.

Mixing is carried out by any of the methods typically used in polyurethane machines. For example, stirrers or screw mixers may be used, although mixing is best carried out by high-pressure injection mixing in which the necessary quantity of mixture per molding is produced in the so-

called shot time.

CLAIMS

1. A process for the production of elastomeric polyurethanes, more particularly in the form of shoe soles, by reaction of a polyurethane reaction mixture of polyol, isocyanate, crosslinking agents and, optionally, catalysts, blowing agents and other additives which are mixed with one another, characterized in that the components polyol, isocyanate and crosslinking agent are delivered in separate lines to a mixing chamber and are only combined and mixed together in the mixing chamber.
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2. A process as claimed in claim 1, characterized in that catalysts and/or blowing agents are also separately delivered and are only mixed with the other components in the mixing chamber.
10
3. A process as claimed in claim 1 or 2, characterized in that the processing temperature of the polyol component is between 60 and 150°C.
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4. An elastomeric polyurethane produced by the process as claimed in any of claims 1 to 3.
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5. A shoe sole produced by the process as claimed in any of claims 1 to 3.

Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

92113.0

Relevant Technical fields

(i) UK CI (Edition K) C3R

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

Date of Search

(ii) ONLINE DATABASE: WPI

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Documents considered relevant following a search in respect of claims

1 TO 5

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	GB 0994479 (DAYCO) see whole specification and Figure 1	1, 2
A	GB 0860135 (HUDSON FOAM) see claims, Figure 1, page 3 lines 49-62	1
A	GB 0820266 (BAYER)	1
A	GB 0845206 (ICI) see claims; page 2 lines 80-105; drawing	1, 2
X	EP 0102709 A1 (EX-CELL-O CORP) see whole specification	1, 4
A	EP 0368270 A (KLOCKNER)	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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